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7883

(12) UK Patent Application (19) GB (11) 2 158 080 A

(43) Application published 6 Nov 1985

(21) Application No 8505279

(22) Date of filing 1 Mar 1985

(30) Priority data

(31) 8405521

(32) 2 Mar 1984

(33) GB

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(51) INT CL⁴
C08G 65/32 C11D 1/722 3/075

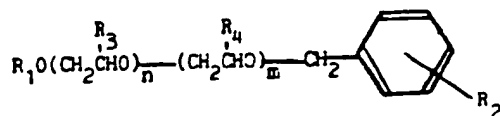
(52) Domestic classification
C3R 27K8E J
C5D 6A5B 6A5D2 6A5E 6B11A 6B12H 6B12N2 6B1 6B2
6C6 6C8
U1S 1379 1427 C3R C5D

(56) Documents cited
None

(58) Field of search
C2C
C3R

(54) End-blocked nonionic surfactants

(57) Alkylbenzyl poly(oxyalkylene) derivatives of the formula



wherein R_1 is a straight or branched chain 1-4C alkyl group; R_2 is a straight or branched chain 4-20C alkyl group; R_3 and R_4 are each, independently, H or CH_3 ; n and m are each integers wherein $n + m$ does not exceed 20 have good nonionic surface activity, biodegradability and are stable to caustic powders. The compounds are useful in alkaline cleaning compositions, such as dishwasher products, and also in rinse-aid formulations for use in automatic dishwashers.

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SPECIFICATION

End-blocked nonionic surfactants

5 The present invention relates to end-blocked nonionic surfactants. More particularly, it relates to new alkylbenzyl poly(oxyalkylene) derivatives useful as nonionic surfactants. 5

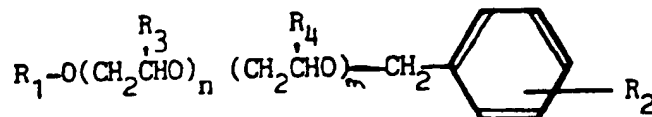
In the past, a number of classes of compounds have been used, in detergents and janitorial compositions, as non-ionic surface active agents. Examples of these include amine ethoxylate propoxylates, benzyl-blocked alkylphenol alkoxyates and ethylene oxide-propylene oxide block copolymers. These materials 10 suffer the major disadvantage that they lack biodegradability and are unstable on solid caustic soda. Furthermore, such materials as are commercially available are ill-defined or have incompletely characterisable chemical structure. 10

In an attempt to overcome the problem of lack of biodegradability of prior nonionic surfactants, alcohol ethoxylate propoxylates, having molecular weights less than 1000, were used. Unfortunately, these 15 materials have poor dispersibility in water at temperatures above their cloud points. In addition, they are unstable in the presence of solid caustic powders, e.g. caustic soda, as in the case of the earlier nonionics. 15

Further attempts to overcome the drawbacks of the prior art materials involved "blocking" the terminal hydroxyl group in fatty alcohol ethoxylates with alkyl chlorides. The procedures used, however, were difficult and they made use of toxic and expensive materials. Similarly blocked non-ionics using benzyl 20 chloride as alkylating agent were introduced although the commercial product was only about 70% blocked, indicating the poor efficiency of the blocking procedure. 20

We have now discovered a range of compounds having good nonionic surface activity which are biodegradable and stable to caustic powders. Furthermore, we have discovered that these compounds can be prepared by a process which achieves greater than 90% blocking.

25 The present invention provides new compounds which are represented by the following general formula I. 25

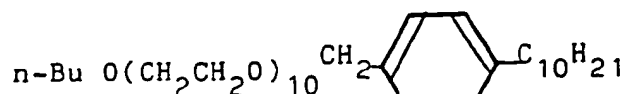
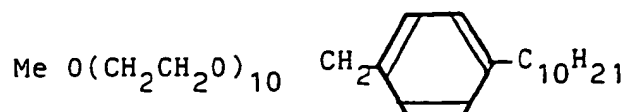
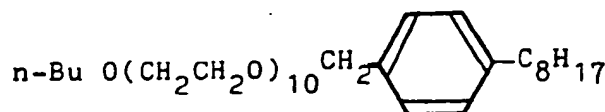
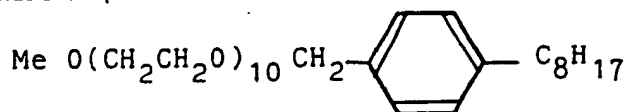


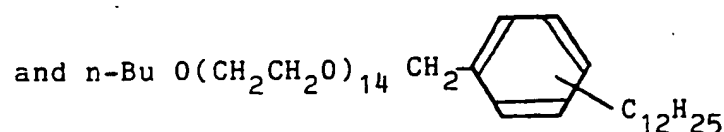
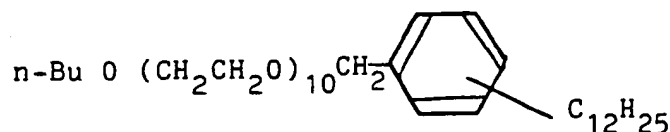
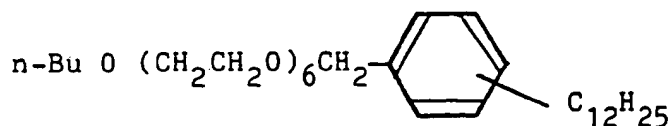
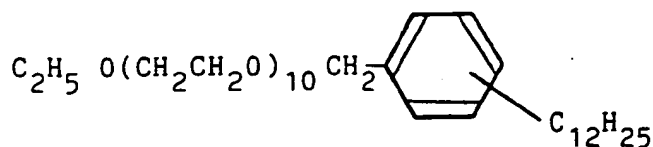
30 wherein R_1 is a straight or branched chain alkyl group having from 1 to 4 carbon atoms; R_2 is a straight or branched chain alkyl group having from 4 to 20 carbon atoms; R_3 and R_4 are each, independently, H or $-\text{CH}_3$, and n and m are each integers wherein the sum $n + m$ is not greater than 20. 30

As we have stated above, the group R_1 is a 1 to 4 C alkyl, such as methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl. The alkyl group R_2 attached to the phenyl ring of the blocking group is a 35 straight or branched chain group containing from 4 to 20 carbon atoms, preferably 8 to 12 carbon atoms. Preferred examples of suitable R_2 groups include straight and branched chain octyl, decyl and dodecyl groups. A particularly preferred R_2 group is n-dodecyl. 35

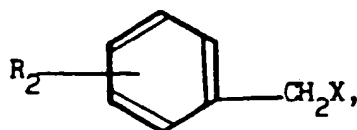
The sum $n + m$ is not greater than 20 and will usually lie within the range of from 5 to 15, more particularly 40 within the range 8 to 14. A preferred value of $n + m$ is 10. 40

Some preferred compounds of the present invention are as follows:





The present invention also provides a process for preparing a compound of the formula I above which process comprises reacting a lower alcohol of the formula R_1OH , wherein R_1 is as defined above, with an alkylene oxide selected from ethylene oxide and propylene oxide, and then reacting the ethoxylated and/or propoxylated material with an alkylbenzyl halide having the formula



wherein X is a halogen atom, preferably a chlorine atom. In a preferred embodiment, the ethoxylated and/or propoxylated material is reacted with a mixture of alkylbenzyl chlorides, such as a mixture of C_8 and C_{10} alkylbenzyl chlorides to give a mixture of reaction products.

If it is desired to form a compound of formula I wherein R_3 is H and R_4 is $-\text{CH}_3$, then the lower alcohol is first reacted with ethylene oxide and the ethoxylated product is then reacted with propylene oxide. If the desired compound of formula I has $\text{R}_3=\text{CH}_3$ and $\text{R}_4=\text{H}$, then the alcohol is first propoxylated and the alkyl propoxylate is then ethoxylated. The amount of reactants used in this step, of course, depend upon the desired values of n and m in the final compound. Usually, the amounts of alkylene oxide used will be sufficient such that the sum of n + m is within the range of from 5 to 15. The alkoxyated lower alcohol is then condensed with the alkylbenzyl chloride. The condensation reaction will usually be conducted in the presence of an alkali metal hydroxide, typically NaOH. The condensation reaction is preferably phase transfer catalysed with, for instance, a catalytic amount of a tetraalkyl ammonium halide. By the use of this process, it is possible to achieve a blocking efficiency of greater than 90%. Furthermore, it should be noticed that, in the above-described process, end-blocking of the molecule and the introduction of the hydrophobe into the molecule are carried out in one step unlike prior art processes. Thus, by the process of the invention, it is possible to make end blocked non ionics at low cost.

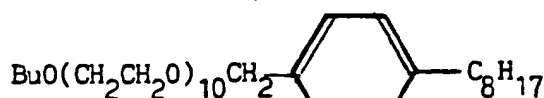
The compounds of the invention have relatively low molecular weight and meet E.E.C. legislation on biodegradability (Directive 82/242/EEC). They are stable on solid caustic powders and have excellent defaming properties, good wetting and detergency. The compounds of the invention are, therefore, particularly well suited to use in strongly alkaline cleaning compositions in combination with solid caustic powders, such as powdered caustic soda. In particular, the compounds of the present invention are especially useful as low-foaming or anti-foaming ingredients in alkaline powder dishwashing products. They may also be used advantageously in rinse-aid formulations for automatic dishwashing and may control or prevent foam generated by or stabilised by food soils.

Example 1

1 mold of n-butanol was ethoxylated with 10 moles of ethylene oxide by a conventional method. The ethoxylated product (150 g) was then charged together with 50% caustic soda solution (80 g) and, as catalyst, benzyltriethylammonium chloride (2.5 g). The temperature of this mixture was raised to 90-95°C at which temperature a mixture of n-octyl and n-decylbenzyl chloride (45 g) was run in over a period of 3 hours. The

reaction mixture was then heated to 110°C and maintained at that temperature for 1 hour. After cooling, the reaction mixture was washed with water to remove salt, unreacted polyglycol and catalyst. The product comprised a mixture of:-

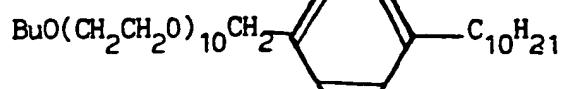
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and

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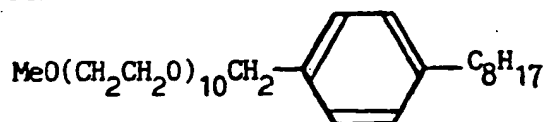
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Example 2

The procedure of Example 1 was repeated, except that methanol, instead of n-butanol, was used. The product comprised a mixture of

15

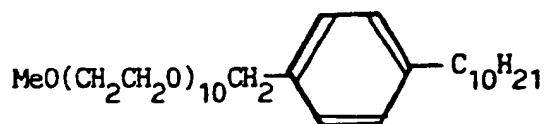
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20

and

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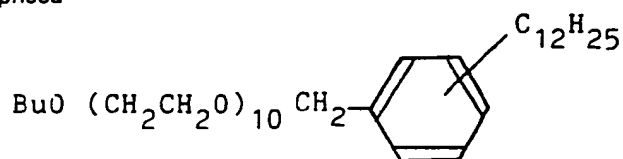
Example 3

The procedure of Example 1 was repeated except that dodecyl benzyl chloride, instead of p-octyl and p-decyl benzyl chloride, was used.

30

The product comprised

35



35

Some of the properties of the products obtained in Examples 1, (A), and 2, (B), were measured and compared with those obtained for a prior art unblocked non-ionic surfactant, nonyl phenol 9.5 mole ethoxylate (NP 95). These are set out below.

40

		A	B	NP95	
45	1. Cloud point, at concentration of 1% in water, in °C	34	47	52	45
	2. Foam (by Ross Miles), at a concentration of 0.1% in water and temperature 5°C below cloud point, in mm.	41	61	100	
50	3. Foam at cloud point, at concentration of 0.1% in water, in mm.	30	28	66	50
	4. Wetting (by Draves) at a concentration of 0.1% in water and temperature 5°C below cloud point, in seconds	11	21	4	
55	5. Stability on caustic	good	good	very poor.	55

These results show that the compositions A and B, which are in accordance with the present invention, show a big foam reduction compared to the prior art compound and suffer only small losses in wetting properties.

60

The compounds of this invention are advantageously used as low-foaming or antifoaming ingredients in alkaline powder dishwashing products.

Example 4

An alkaline powder dishwashing product with good cleaning power and controlled foaming characteristics is prepared by blending the following:

5	Sodium metasilicate	30%	by weight	5
	Soda ash	38%	by weight	
	*Trisodium nitrilo triacetic acid powder	10%	by weight	
	Sodium tripolyphosphate	20%	by weight	
	Suitable compound of present invention	2%	by weight	

10
*e.g. Nervanid NTA Conc. Powder, a trade name of A.B.M. Chemicals Ltd. 10

wherein the suitable compound of the present invention is one or a mixture of more than one of the following:

- 15
a) A compound according to formula 1 wherein
(n + m) = 10 and
R₃ = R₄ = H and R₁ = C₂H₅ and R₂ = C₁₂H₂₅ 15
- 20
b) a compound according to formula 1 wherein
(n + m) = 6 and
R₃ = R₄ = H and R₁ = C₄H₉ (n-butyl) and R₂ = C₁₂H₂₅. 20
- 25
c) a compound according to formula 1 wherein
(n + m) = 14 and
R₃ = R₄ = H and R₁ = C₄H₉ (n-butyl)
and R₂ = C₁₂H₂₅. 25

The compounds of the invention are advantageously used in rinse-aid formulations for automatic dishwashing. Spotless quick-drying is achieved without causing subsequent foaming problems in those machines where rinse water is re-cycled into the wash-water. Furthermore formulations containing compounds of the present invention may control or prevent foam generated or stabilised by food soils. 30

Example 5

Rinse aid formulations for automatic dishwashing according to the following recipes give spotless quick-drying: 35

40	Suitable compound of present invention	25%	40
	Dipropylene glycol	10%	
	N-lauroyl sarcosinate	1%	
	Water	64%	

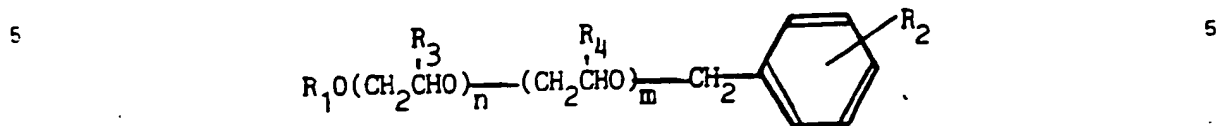
Where a suitable compound of the present invention includes a mixture of compounds according to formula 1, wherein, for example, (n + m) = 6 and 14 and R₃ = R₄ = H and R₁ = C₄H₉ (n-butyl) and R₂ = C₁₂H₂₅. Such mixture comprises 60% of such compound wherein (n + m) = 14 and 40% of such compound wherein (n + m) = 6, and when the formulation of Example 5 is made with this mixture of non-ionic surface active agents a formulation (Formulation 1) with properties superior to those of current commercial formulations is obtained, as measured in the following tests: 45

50		Actives % (Drying at 110°C)	Protein* Foam (mm)	Haze Temp. (°C)	Dispersibility in water at 80°C	Glass rinse appearanc at 80°C	50
	Formulation 1	36	24	61	Excellent	Excellent	
55	Commercial Product A	30	184	51	Fair	Very good	55
	Commercial Product B	50	50	60	Good	Fair	
	Commercial Product C	32	90	47	Good	Fair	

* Protein foam tests measure the height of foam produced in a dynamic foaming test with 100 ppm of rinse aid in water of 150 ppm hardness in the presence of 0.25% milk protein and 0.36% alkaline builders at a temperature of 60°C. The test involves pumping the test solution at a pressure of 5 psi through a 1.8 mm orifice with a fall of 750 mm onto the surface of the test solution with recirculation for 5 min. 60

CLAIMS

1. A compound which is represented by the following general formula:-



- 10 wherein R_1 is a straight or branched chain 1-4C alkyl group; R_2 is a straight or branched chain 4-20C alkyl group; R_3 and R_4 are each, independently, H or $-CH_3$; and n and m are each integers wherein the sum $n + m$ is not greater than 20.

2. A compound as claimed in claim 1, wherein R_2 is a straight or branched chain alkyl group having from 8 to 12 carbon atoms.

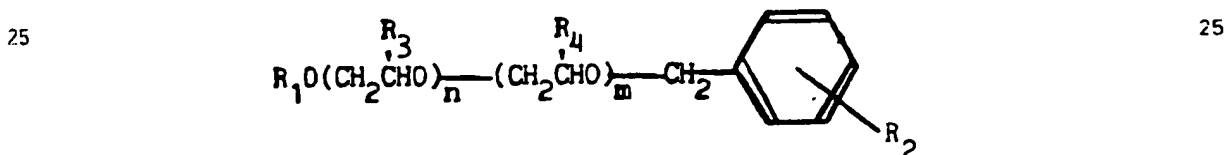
- 15 3. A compound as claimed in claim 2, wherein R_2 is a straight or branched chain octyl, decyl or dodecyl group.

4. A compound as claimed in any one of claims 1 to 3, wherein the sum of $n + m$ is in the range of from 5 to 15.

5. A compound as claimed in any one of claims 1 to 4, wherein R_1 is n-butyl; R_2 is a substantially linear dodecyl; R_3 and R_4 are both H and the sum $n + m$ is in the range of from 5 to 15.

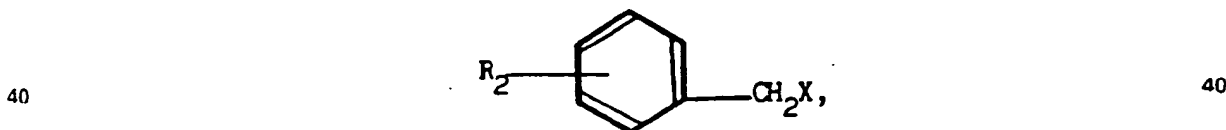
6. A compound as claimed in any one of claims 1 to 4, wherein R_1 is ethyl; R_2 is a substantially linear dodecyl; R_3 and R_4 are both H and the sum $n + m$ is in the range of from 5 to 15.

7. A method of preparing a compound having the following general formula:-



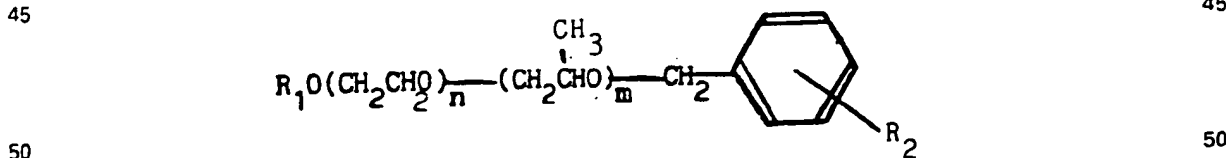
- 30 wherein R_1 is a straight or branched chain 1-4C alkyl group; R_2 is a straight or branched chain 4-20C alkyl group; R_3 and R_4 are each, independently, H or $-CH_3$; and n and m are each integers wherein the sum $n + m$ is not greater than 20,

- 35 which method comprises reacting an alcohol of the formula R_1OH , where R_1 is as defined above, with an alkylene oxide selected from ethylene oxide, propylene oxide and mixtures thereof and then reacting the resulting alkoxyated material with an alkylbenzyl halide having the formula

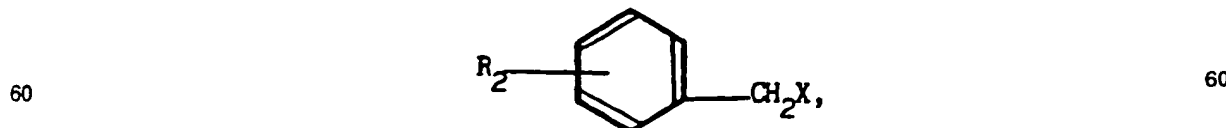


wherein R_2 is as defined above and X is a halogen atom.

8. A method of preparing a compound having the following general formula:-

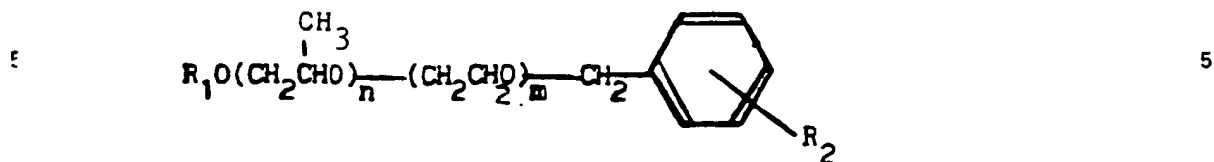


- 55 wherein R_1 is a straight or branched chain 1-4C alkyl group; R_2 is a straight or branched chain 4-20C alkyl group; and n and m are each integers wherein the sum $n + m$ is not greater than 20, which method comprises reacting an alcohol of the formula R_1OH , where R_1 is as defined above, with ethylene oxide, then reacting the resulting ethoxylated product with propylene oxide and then reacting the resulting propoxylated material with an alkylbenzyl halide of the formula:-

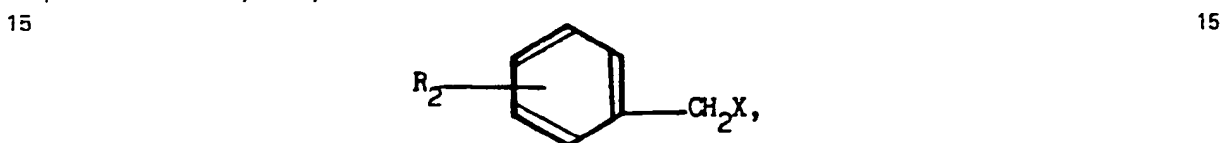


where R_2 is as defined above and X is a halogen atom.

9. A method of preparing a compound having the following general formula:-



10 wherein R_1 is a straight or branched chain 1-4C alkyl group; R_2 is a straight or branched chain 4-20C alkyl group; and n and m are each integers wherein the sum $n + m$ is not greater than 20, which method comprises reacting an alcohol of the formula R_1OH , where R_1 is as defined above, with propylene oxide, reacting the resulting propoxylated material with ethylene oxide and then reacting the resulting ethoxylated product with an alkylbenzyl halide of the formula



20 wherein R_2 is as defined above and X is a halogen atom.

10. A cleaning composition comprising a mixture of caustic soda and at least one compound as claimed in claim 1.

11. A cleaning composition substantially as hereinbefore described in Example 4.

25 12. A rinse aid formulation for use in an automatic dishwasher substantially as hereinbefore described in Example 5.

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